

Challenges in Development of Sustainable Carbon Dioxide Mitigation Technology for Closed Loop ECLSS for Long Duration Human Space Missions

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EXTENDED ABSTRACT

Introduction:

Long duration manned space travel explicitly demands design of effective artificial CO₂ mitigation system for meeting the necessity of human comfort inside crew cabin. The cost and mass optimization for achieving effective sizing of environment control and life support system (ECLSS) need complete closure of all relevant material loops. One of the critical aspects of the closed-loop ECLSS is effective mitigation of carbon dioxide generated by metabolic activity of the astronauts. Carbon dioxide mitigation/management involves selectively capturing/storing carbon dioxide gas from the atmosphere of the crew cabin and subsequently converting it into useful products in the most efficient way.

In the past two decades, various kind of studies were conducted over the globe on the catalytic methanation route of carbon dioxide (CO₂). This reaction has drawn attention of researcher due to its specific interest of industrial pollution control of carbon dioxide which is one of the major greenhouse gases. However, very limited studies have been reported on the use of CO₂ methanation reaction process for the development of an artificial life support system for human space mission. Alptekin, *et.al.* successfully demonstrated a working of the prototype model of the 'Sabatier reactor' in conjunction with molecular sieve adsorbent bed based CO₂ removal assembly with Sabatier reactor facilitated with vacuum/thermal desorption and compression which enables reduction of CO₂ into methane (CH₄) and water [1]. Studies were conducted on micro reactor based carbon dioxide reduction assembly loaded with ruthenium (Ru) supported on titania (TiO₂) and Ru supported on zirconia (ZrO₂) catalysts towards the CO₂ methanation reaction activity at temperatures from 110° to 350°C by Vander Wiel, *et. al.* They reported strong influence of residence time on conversion for 3wt% ruthenium (Ru) based catalyst which exhibits nearly 100% selectivity towards methane [2]. Wang, *et.al.*, in their critical review in the area of catalytic reactivity, reactor innovation, and reaction mechanism emphasized about the superiority of ruthenium (Ru) and rhodium (Rh) supported on alumina (Al₂O₃) catalyst over other catalysts towards achieving higher methane selectivity [3].

This paper specifically emphasizes on the efficiency of the CO₂ reduction experiments carried out over Ru-γ-Al₂O₃ catalyst using a laboratory set up under different conditions of volumetric flow rates inside the reactor, reactant molar ratio and temperature.

Experimental:

The Ru- γ -Al₂O₃ catalyst was tested for carbon dioxide hydrogenation reaction under various reaction conditions. The schematic representation of the reactor set up used in the study is as shown in the Figure 1.

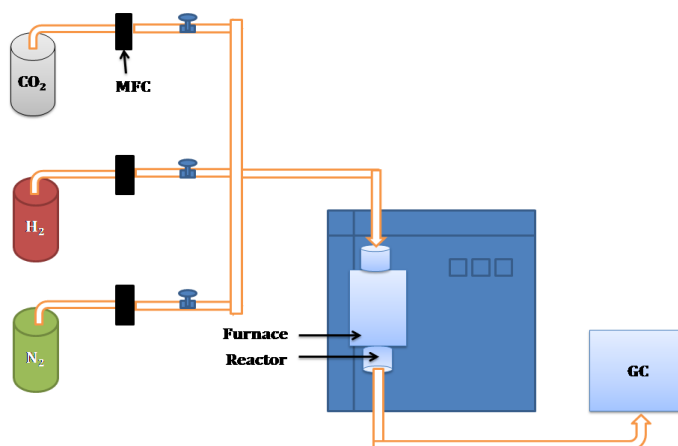


Figure 1: Schematic representation of CO₂ methanation reactor set up

The catalyst bed L/D is 55 mm/22.5 mm. The powder catalyst was pressed into pellets and crushed and sieved to size 0.5 mm. 0.3 g of these particles is placed in the middle of a steel reactor tube (length 60 cm, ID 22,5 mm) provided with a thermo-well to measure the bed temperature. Ceramic beads and ceramic wool are filled below and above the catalyst bed to improve thermal conductivity and gas mixing. The catalyst bed is separated from the ceramic beads by a thin layer of ceramic wool.

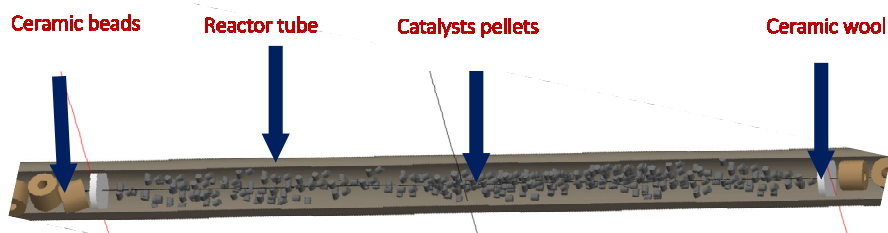
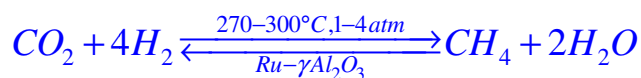


Figure 2: Schematic of the catalytic reactor tube for CO₂ hydrogenation

The stoichiometric reaction among CO₂ and hydrogen forming methane and water is,



Input feed compositions of CO₂:H₂ mole ratios ranging from 1:4 to 1:6 were used. Total flow rate was adjusted to attain different GHSV. Experiments were conducted in the flow rates ranging from 100 ml min⁻¹ to 500 ml min⁻¹ and the temperature range of 30°C to 320°C.

The catalytic testing was carried out at a particular flow (in terms of gas hour space velocity, GHSV) at varying temperatures. This was repeated at varying GHSV's.

A Nucon make gas chromatograph (GC) equipped with TCD detector and porapak (permeable polymer) and molecular sieve column using Ar as carrier gas (50 mL/min) was employed for gas analysis.

CO₂ conversion was calculated by the following equation:

$$\% \text{ of CO}_2 \text{ conversion (X)} = \frac{\text{Conc.of CO}_2 \text{ at RT} - \text{Conc.Of CO}_2 \text{ at diff.temp.}}{\text{Conc.Of CO}_2 \text{ at RT} + \varepsilon_{\text{CO}_2}(\text{Conc.Of CO}_2 \text{ at diff.temp})} \times 100 \quad \text{---(1)}$$

Results and Discussion

Equilibrium Conversion for CO₂ Methanation Reaction:

Equilibrium reaction rate constant (K_{eq}) was computed based thermodynamic properties viz. Gibb's free energy at constant pressure (ΔG^o and heat of reaction (ΔH^o).

$$K_{eq}(T) = \exp \left[\frac{1}{1.987} \left\{ \frac{56000}{T_K^2} + \frac{34633}{T_K} - 16.4 \ln T_K + 0.00557 T_K \right\} + 33.65 \right] \quad \text{---(2)}$$

$$\frac{X_{eq}^3 (1 + \varepsilon_{CO_2} X_{eq})^2}{(1 - X_{eq}) (M - 4X_{eq})^4} = \frac{K_{eq}}{4} (p_{CO_2}^o)^2 \quad \text{----(3)}$$

Where, X_{eq} is an equilibrium conversion, ε is volumetric expansion factor and M is hydrogen to carbon dioxide mole ratio.

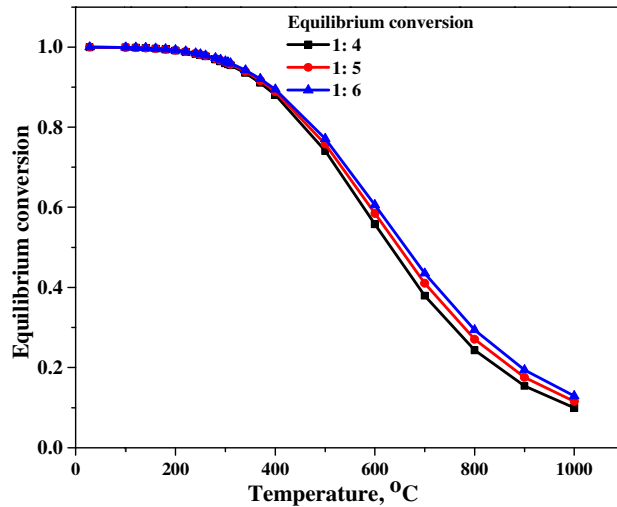


Figure 3: Equilibrium conversion as a function of temperature at different mole ratios of CO₂ and H₂

Effect of mole ratio and reactant flow rate:

Effect of molar ratio between carbon dioxide and hydrogen at different flow rates was studied. Experimental result showed that at a stoichiometric molar ratio of 1:4 for carbon dioxide and hydrogen, the conversion remains at significantly below than that of equilibrium conversion. However, the conversion attains equilibrium value at molar ratio of 1:5 and 1:6 at temperature of 300°C.

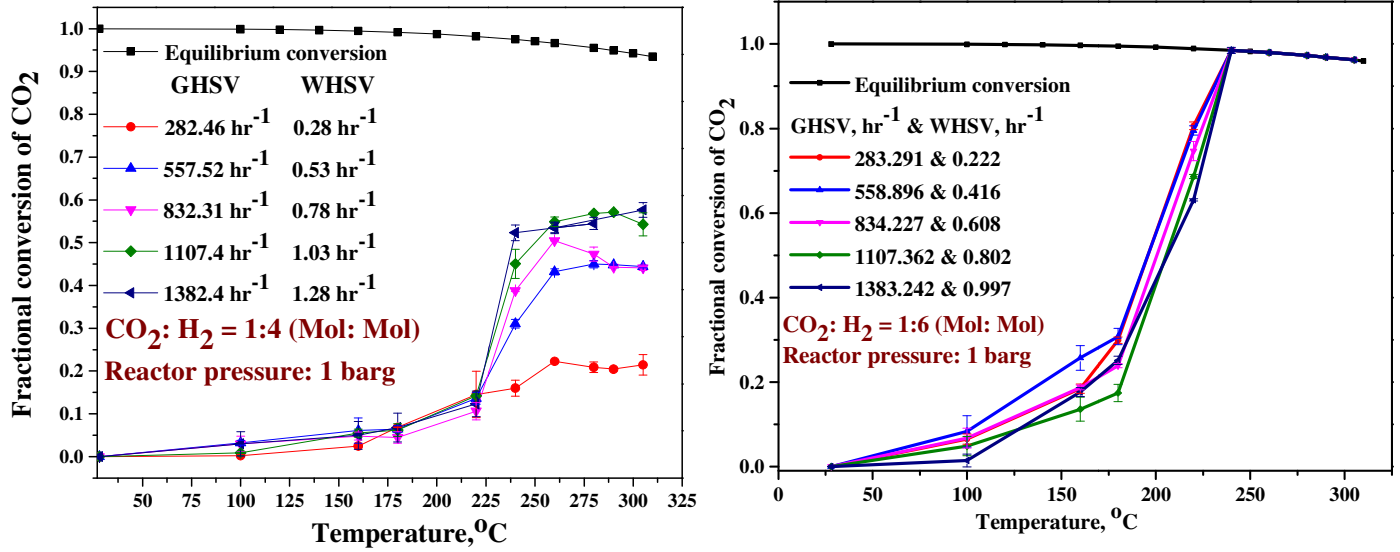


Figure 2: Conversion of CO₂ as function of temperature and flow rate at CO₂:H₂ mole ratios of 1:4 and 1:6

Molar ratio of 1:4 for carbon dioxide and hydrogen exhibited poor approach towards equilibrium whereas, the mole ratios of 1:5 and 1:6 showed remarkable improvement in the conversion reaction with conversion approaching equilibrium levels irrespective of the flow rates or gas hourly space velocity.

Estimation of Global Reaction Rate Parameters and Activation Energy:

Kinetic parameters were computed from the global reaction rate expression using the experimental data of conversion at different temperatures and flow rates. Following global rate equation was adapted for expressing carbon dioxide methanation reaction rate as a function of the reactant partial pressures [4].

$$r_{CO_2} = k_f \left\{ \left[p_{CO_2} \right]^n \left[p_{H_2} \right]^{4n} - \frac{\left[p_{H_2O} \right]^{2n} \left[p_{CH_4} \right]^n}{\left(K_{eq}(T) \right)^n} \right\} \quad \text{---(4)}$$

Design equation for a plug flow reactor is [5],

$$\left(\frac{w}{F_{CO_2}^o} \right) = \int_0^{X_{CO_2}} \frac{dX_{CO_2}}{-r_{CO_2}} \quad \text{----(5)}$$

Substituting equation (4) in equation (5),

$$\left(\frac{w}{F_{CO_2}^o} \right) = \int_0^{X_{CO_2}} \frac{dX_{CO_2}}{k_f^n \left\{ [p_{CO_2}]^n [p_{H_2}]^{4n} - \frac{[p_{H_2O}]^{2n} [p_{CH_4}]^n}{(K_{eq}(T))^n} \right\}} \quad \text{-----}(6)$$

The equation (6) was solved iteratively via numerical integration technique using Polymath software for known values of catalyst weight (w) and initial molar flow rate of carbon dioxide to obtain the kinetic parameters viz. k_f (forward reaction rate constant) and n (catalyst coefficient).

Where k_f can be expressed in the form of Arrhenius equation,

$$k_f^n = k_0^n e^{-\frac{E}{RT}} \quad \text{---}(7)$$

From the plot of $\ln k_f$ and $1000/T$, activation energy (E) and frequency factor (k_0) were evaluated.

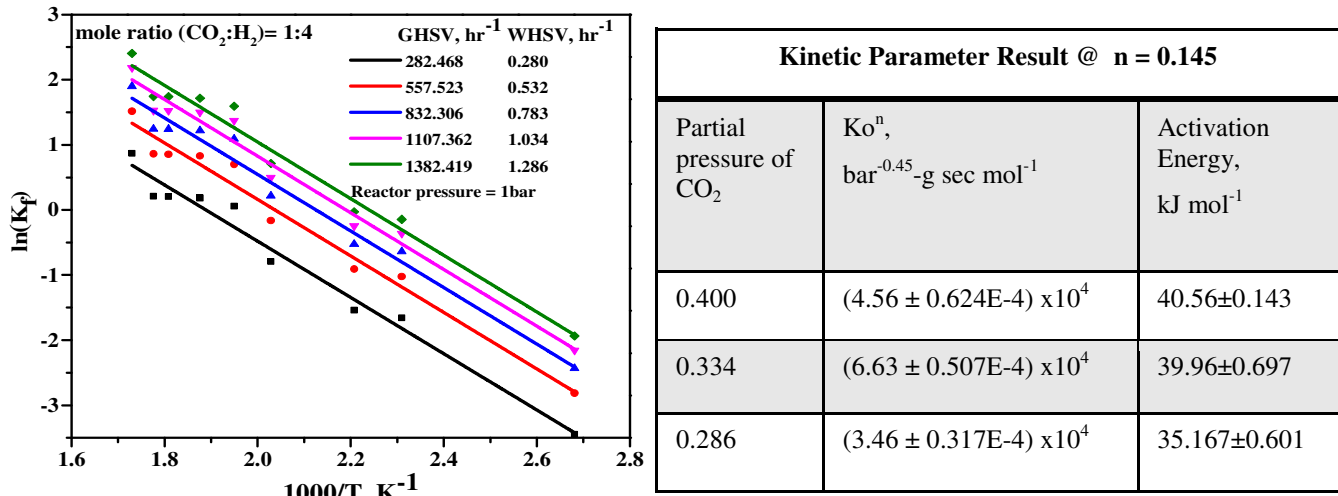


Figure 3: Arrhenius plot for different flow rates

Reactor design strategy: For practical application of the carbon dioxide methanation reactor in a typical crew module housing four astronauts, a reactor sizing was carried out based on the reaction rate correlation with the convective mass flow and geometric parameters.

A correlation between forward reaction rate constant (k_f) and Reynolds number, Schmidt number and dimensionless geometric parameter (dp/D_T – ratio between catalyst particle diameter and reactor tube diameter) was established based on non-linear regression of reaction rate constant obtained at different flow rates [5]. The correlations obtained at different mole ratios are given below (Equation 8, 9 and 10):

For CO₂:H₂ mole ratio of 1:4,

$$k_{obs} = \frac{9.6499 (Re)^{0.6713} (Sc)^{-0.5282} \left(\frac{dp}{Dt} \right)^{-0.9430}}{33.2729 + (Re)^{0.6713} (Sc)^{-0.5282}} \quad \text{-----}(8)$$

For CO₂:H₂ mole ratio of 1:5,

$$k_{obs} = \frac{7.0764(\text{Re})^{1.1582} (\text{Sc})^{1.1570} \left(\frac{dp}{Dt}\right)^{-0.4987}}{234.2464 + (\text{Re})^{1.1582} (\text{Sc})^{1.1570}} \text{-----(9)}$$

For CO₂:H₂ mole ratio of 1:6,

$$k_{obs} = \frac{6.7108(\text{Re})^{1.1374} (\text{Sc})^{1.1468} \left(\frac{dp}{Dt}\right)^{-0.4714}}{199.6594 + (\text{Re})^{1.1374} (\text{Sc})^{1.1468}} \text{-----(10)}$$

The correlation obtained for the mole ratio of 1:5, was used for designing a prototype carbon dioxide reduction reactor for mitigation of 4 kg/day of carbon dioxide exhaled by four astronauts. Conversion efficiency of 90% was considered for sizing the reactor. The catalyst requirement of 241 g was found to meet the requirement of hydrogenating 4 kg/day of carbon dioxide.

Conclusion:

The Ru- γ -Al₂O₃ catalyst was tested for carbon dioxide hydrogenation reaction under various reaction conditions. The strong influence of convective transport of CO₂ molecule to catalytic surface on the reaction conversion was observed from the experimental data. Effect of molar ratio between carbon dioxide and hydrogen at different flow rates was studied. Experimental result showed that, at a stoichiometric molar ratio of 1:4 for carbon dioxide and hydrogen, the conversion remains at significantly below than that of equilibrium conversion. However, the conversion attains equilibrium value at molar ratio of 1:5 and 1:6 at temperature of 300°C.

Based on the strong dependence of reactant flow rate and mol ratio on conversion, an empirical correlation has been established for determination of global reaction rate constant as a function of Reynolds number, Schmidt number and geometric parameter for reactor and catalyst pellet. Further the correlation was used for designing a prototype reactor with a CO₂ reduction capability up to 4 kg/day.

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